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MULTI-LAYERED CARBON NANOBALL FOR DEODORIZATION

TECHNICAL FIELD

The present invention relates to a carbon nanoball for deodorization, and more particularly to a multi-layered carbon nanoball for deodorization, which is composed of a porous carbon shell having a spherical hollow core.

BACKGROUND ART

Generally, various bad smells are generated from daily necessaries such as refrigerator, air conditioner, diaper, hygienic band, cigarette, footwear cabinet and clothes chest and in daily life area such as bedroom, bathroom and automobile room. In addition, bad smells are also generated from exhaust gas of automobiles and industrial equipments such as refuse disposal plant, wastewater disposal plant and factories. Materials generating bad smells are representatively as follows: methanethiol, methyl sulfide, dimethyl disulfide, hydrogensulfide, ammonia, trimethylamine, acetaldehyde, nitric oxide, nitrous oxide, styrene and so on.

Also, various kinds of deodorizing agents have been developed in order to eliminate such bad smells.

Recently, a method for making a carbon nanoball composed of a porous carbon shell having a spherical hollow core (*Adv. Mater. 2002, 14, no. 1, January 4*) was proposed. This carbon nanoball has an advantage that it may adsorb more various kinds of malodor substances than a conventional activated carbon deodorizing agent. However, the carbon nanoball has some limitations that it may not adsorb any more malodor substances after adsorbing a certain amount. In addition, the above-mentioned carbon nanoball has a limited capacity in deodorizing.

DISCLOSURE OF INVENTION

The present invention is designed to solve such drawbacks of the prior art, and therefore an object of the present invention is to provide a carbon nanoball having excellent deodorizing ability and capable of adsorbing various kinds of malodor substances.

In order to accomplish the above object, the present invention provides a carbon nanoball for deodorization comprising a porous carbon shell having a spherical hollow core, wherein at least one deodorizing material selected from the group consisting of transition metal, oxidized transition metal and alkali metal salt is impregnated to the shell, wherein the porous carbon shell has a multi-layered structure in which at least two layers having different pore sizes are included, and wherein an average diameter of pores formed in an outer layer is larger than an average diameter of pores formed in an inner layer or vice versa.

Preferably, the transition metal is one selected from the group consisting of Copper (Cu), Iron (Fe), Manganese (Mn), Nickel (Ni), Cobalt (Co), Silver (Ag), Gold (Au), Vanadium (V), Ruthenium (Re), Titanium (Ti), Chrome (Cr), Zinc (Zn) and Palladium (Pd), and the alkali metal salt is one selected from the group consisting of sodium bromide (NaBr), sodium iodide (NaI), potassium bromide (KBr), potassium iodide (KI) and potassium iodate (KIO_3).

BRIEF DESCRIPTION OF THE DRAWINGS

These and other features, aspects, and advantages of preferred embodiments of the present invention will be more fully described in the following detailed description, taken accompanying drawings. In the drawings:

FIG. 1 is a schematic diagram for illustrating the process for making a carbon nanoball for deodorization according to the present invention;

FIG. 2 is a photograph of a multi-layered carbon nanoball according to the present invention, taken by an electronic microscope; and

FIG. 3 is a graph dynamic absorption behavior of the multi-layered carbon nanoball for deodorization according to the present invention.

BEST MODES FOR CARRYING OUT THE INVENTION

Hereinafter, embodiments of the present invention will be described, however the present invention is not limited to the following embodiments, but capable of being modified in diverse ways within the scope of the invention.

A carbon nanoball for deodorization of the present invention has a ball-shaped carbon structure composed of a hollow core and a porous shell. Transition metal, oxidized transition metal, alkali metal salt or their mixture is impregnated to the shell. In addition, the porous carbon shell has at least two layers of different pore sizes. Pores formed in the outer layer of the shell can have an average diameter larger than pores formed in the inner layer or vice versa, so various kinds of malodor substances may be absorbed in order depending on their size, shape or chemical characteristics. The size of the pores is controlled in the range of 0.01 to 50nm.

Since the shell has at least two layers of different pore sizes, various kinds of malodor substances may be absorbed, and the deodorizing materials impregnated in the pores and on the inner and outer surfaces of the shell may chemically adsorb and destroy the malodor substances. This carbon nanoball for deodorization of the present invention shows more excellent deodorizing ability than the impregnated activated carbon disclosed in Korean Laid-open Patent Publication No. 1999-80808. In other words,

since the activated carbon has microporous pores, the pores may be clogged to deteriorate the deodorizing ability when the deodorizing materials are impregnated. However, since the carbon nanoball for deodorization of the present invention has the mesoporous pores in the shell, such a problem does not occur. In addition, since the carbon nanoball for deodorization of the present invention captures the malodor substances in the hollow core thereof, differently to the impregnated activated carbon, it is possible to give sufficient contact time between the malodor substances and the deodorizing material impregnated on the inner surface of the shell. In addition, the carbon nanoball of the present invention may prevent secondary pollution caused when decomposition products generated by the deodorizing materials are emitted outside.

A method for making the carbon nanoball for deodorization according to the present invention is described in detail with reference to FIG. 1.

At first, a spherical silica core 1 is prepared. The silica core 1 may be composed according to the well-known Stober method (*Stober, W.; Fink, A.; Bohn, E. J. Colloid Inter. Sci. 1968, 26, 62*) from a silica precursor such as tetramethylorthosilicate and tetraethylorthosilicate, as an example. The silica core preferably has a diameter of 5 to 1,000nm.

After that, a first shell 2 made of silica and surface active agent is grown up on the surface of the silica core 1 by reacting silica precursor and surface active agent such as alkyltrimethoxysilane expressed by the following Chemical Formula 1, alkyltriethoxysilane expressed by the following Chemical Formula 2, halogenated alkyltrimethyl ammonium expressed by the following Chemical Formula 3, alkylpolyoxyethylene expressed by the following Chemical Formula 4 and glycerolethoxylate expressed by the following Chemical Formula 5, in a solvent.

Chemical Formula 1

$R_1R_2R_3R_4Si(OCH_3)_3$

In the Chemical Formula 1, R_1, R_2 and R_3 are methyl or ethyl groups independently, and R_4 is an alkyl group having a carbon number of 12 to 22.

Chemical Formula 2

$R_1R_2R_3R_4Si(OC_2H_5)_3$

In the Chemical Formula 2, R_1, R_2 and R_3 are methyl or ethyl groups independently, and R_4 is an alkyl group having a carbon number of 12 to 22.

Chemical Formula 3

$R_1R_2R_3R_4NX$

In the Chemical Formula 3, R_1, R_2 and R_3 are independently methyl or ethyl groups, R_4 is an alkyl group having a carbon number of 4 to 22, and X is halogen.

Chemical Formula 4

$R(OCH_2CH_2)nOH$

In the Chemical Formula 4, R is an alkyl group having a carbon number of 4 to 22, and n is an integer in the range of 3 ~ 20.

Chemical Formula 5

$$CH_2(CH_2O)n_1HCH(CH_2O)n_2HCH_2(CH_2O)n_3H$$

In the Chemical Formula 5, n_1, n_2 and n_3 are independently integers in the range of 4 ~ 20.

Then, silica precursor and surface active agent having different kind and molar ratio are added and reacted to form a second shell 3 on the surface of the first shell 2. The size of pores formed in the shell is changed depending on the kind of the surface active agent and the kind and molar ratio of the silica precursor. Thus, the kinds of silica precursor and surface active agent are controlled so that the pores formed in the second shell 3 have a larger size than the pores formed in the first shell 2. When required, a third shell having larger pores may be subsequently formed on the surface of the second shell 3.

After that, after the product in which the shell is formed is selectively filtered and then calcined at, for example, 500 ~ 600°C to remove the surface active agent components. Then, a particle 10 having a multi-layered silica shell 4 in which mesoporous pores having a certain size are formed in the place where the surface active agent is removed is obtained. The multi-layered silica shell 4 preferably has a thickness of 10 to 500nm.

Subsequently, a monomer 11 such as acrylonitrile, phenol-formaldehyde and divinylbenzene, sugar, furfuryl, and so on, which are capable of forming polymer as a carbon precursor, is injected into the pores formed in the shell of the particle 10 in which the multi-layered silica shell is formed. After that, the monomer is polymerized to form a polymer. As an example of polymerization, when the radical polymerization is

utilized to form a polymer as a carbon precursor, the monomer is sufficiently mixed with a radical initiator and then injected into the mesoporous pores of the silica particle, and then polymerized according to the characteristics of the monomer. At this time, azobisisobutyronitrile (AIBN), t-butyl peracetate, benzoyl peroxide, acetyl peroxide and lauryl peroxide may be used for the radical initiator. This polymerization is well known in the art, and preferably conducted for about 12 hours at 60 to 130°C to make the silica/polymer composite.

And then, the silica/polymer composite is treated under the nitrogen atmosphere at about 1,000°C so as to make the silica containing a carbonized polymer 13. After that, the silica/polymer composite is put into a hydrofluoric acid solution or a sodium hydroxide/ethyl alcohol mixed solution to remove the silica structure, then a carbon nanoball 20 which has a spherical hollow core 15 and a porous carbon shell is obtained.

After that, the carbon nanoball 20 is dipped into a deodorizing material solution composed of transition metal, oxidized transition metal, alkali metal salt or their mixture and matured at the room temperature for 2 to 3 days, and then filtered and dried at 70 to 110°C to make the multi-layered carbon nanoball to which the deodorizing material 17 is impregnated according to the present invention. As for the transition metal or the oxidized transition metal which may be impregnated to the shell, Copper (Cu), Iron (Fe), Manganese (Mn), Nickel (Ni), Cobalt (Co), Silver (Ag), Gold (Au), Vanadium (V), Ruthenium (Re), Titanium (Ti), Chrome (Cr), Zinc (Zn), Palladium (Pd) or their oxide may be used. As for the alkali metal, sodium bromide (NaBr), sodium iodide (NaI), potassium bromide (KBr), potassium iodide (KI) and potassium iodate (KIO_3) may be used. An impregnated amount of the deodorizing material 17 may be controlled by changing the concentration of the deodorizing material solution or the infiltration time, and is preferably in the range of 0.01 ~ 30 wt% on the basis of the total weight

of the carbon nanoball for deodorization.

The carbon nanoball impregnated by the deodorizing material according to the present invention may be provided with one or more kinds of deodorizing materials am ong the above-mentioned metals. Thus, the deodorizing agent containing the carbon nanoball impregnated by the deodorizing material according to the present invention m ay be prepared or composed in various ways depending on the kind of bad smell or its usage. For example, the deodorizing agent may contain carbon nanoball to which onl y one kind of deodorizing material is impregnated, or to which two different kinds of d eodorizing materials are impregnated, or more than two kinds of deodorizing materials are impregnated.

The carbon nanoball impregnated by the deodorizing material according to the present invention may be used for deodorizing and eliminating various odor materials such as methanethiol, methyl sulfide, dimethyl disulfide, hydrogen sulfide, ammonia, t rimethylamine, styrene, acetaldehyde, nitric oxide, nitrous oxide, indoor bad smells ge nerated in bathroom, kitchen or footwear cabinet in home, and smell of tobacco. Thu s it also may give excellent effects in eliminating bad smells of refrigerator, air conditi oner, air cleaner, automobile room, exhaust gas of cars as well as a human body.

In addition, the carbon nanoball impregnated by the deodorizing materials acco rding to the present invention may be uniformly dispersed and stuck to one having a sh ape of sheet, pack or pad, thus it may be applied to goods such as a diaper for the infan t or the person suffered from the incontinence or a hygienic band for women, which us e such matters.

Embodiment 1 to 8

A spherical silica core is composed according to the well-known Stober metho

d by using tetraethoxysilane as a silica precursor. At this time, 60mL of tetraethoxysilane is put into a homogeneous mixture solvent including 1000mL of ethanol, 80mL of water and 40mL of 28% concentration aqueous ammonia to form a spherical silica core of 200 to 300nm.

Then, 59mL of mixture in which octadecyltrimethoxysilane (C_{18}-TMS) and tetraethoxysilane are mixed at a molar ratio of 11.8, which is a surface active agent, is put into 1180mL of silica core and then reacted to grow the first shell on the surface of the silica core. And then, 59mL of mixture in which octadecyltrimethoxysilane and tetraethoxysilane are mixed at a molar ratio of 47.2 is additionally put therein and reacted for growing the second shell. Subsequently, the composed silica particle is filtered and then thermally treated at 550°C for 5 hours so that mesoporous pores having a certain size are formed in the place where the surface active agent is removed.

Then, divinylbenzene is sufficiently mixed with azobisisobutyronitrile (AIBN), which is a radical initiator, and then injected into the mesoporous pores of the silica particle, and then polymerized at 80°C for about 12 hours to make a silica structure containing polymer. In succession, the silica structure containing polymer is carbonized under the nitrogen atmosphere at 1,000°C to form a carbon nanoball. Subsequently, the carbon nanoball is put into hydrofluoric acid to remove inorganic structure of the carbon nanoball, so the carbon nanoball having a ball-shaped carbon structure including a hollow core and a porous multi-layered shell is obtained.

After that, in order to impregnate the deodorizing materials of the following Table 1, the carbon nanoball made along with the above-mentioned method is dipped into 1N of the deodorizing material solution for about 50 hours, then filtered and dried at 70°C, so a carbon nanoball impregnated by the deodorizing materials is obtained.

Table 1

	The kind of impregnated metal (impregnated amount of metal, %)
Embodiment 1	copper (1.3) + manganese (0.3)
Embodiment 2	nickel (3.1) + iron (0.8)
Embodiment 3	gold (0.8) + chrome (0.9) + palladium (0.8)
Embodiment 4	copper (3.1) + iron (0.8) + zinc (0.8)
Embodiment 5	potassium iodide (3.4)
Embodiment 6	silver (4.2)
Embodiment 7	cobalt (2.1) + potassium iodate (1.3)
Embodiment 8	vanadium (2.1) + ruthenium (0.3) + titanium (0.6)

In Table 1, Impregnated Amount (%) of Metal = Weight of Metal/Weight of C arbon nanoball × 100.

Comparative Examples 1 and 2

Carbon nanoballs which mainly includes impregnated activated carbon as a deo dorizing material, manufactured by S company and L company are selected as compar ative examples 1 and 2.

Deodorizing abilities against methanethiol of the carbon nanoballs according to the embodiment 5 and the comparative examples 1 and 2 are compared, and the comp arison results are shown in FIG. 3. Methanethiol of 50 ppm is passed at a rate of 100 mL/min through a reactor containing the deodorizing materials, and its dynamic absor ption behavior according to time is analyzed with a mass spectrometer. Referring to FIG. 3, it would be understood the carbon nanoball impregnated by the deodorizing ma terials, which has a multi-layered shell structure according to the present invention, sh ows continuously excellent deodorizing effects rather than the comparative examples.

INDUSTRIAL APPLICABILITY

As described above, the multi-layered carbon nanoball impregnated by deodorizing materials according to the present invention adsorbs various kinds of malodor substances as well as shows good deodorizing ability. Thus, the carbon nanoball of the present invention may show excellent deodorizing effect in capturing and resolving the malodor substances when it is used as a deodorizing agent in various odorizing daily necessaries, living spaces, industrial spots and other various stink-generating circumstances.

The present invention has been described in detail. However, it should be understood that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.